

TITLE

**Flame Retardant Fiber Blends Comprising Flame Retardant
Cellulosic Fibers and Fabrics and Garments Made Therefrom**

BACKGROUND OF THE INVENTION

- 5 There is an ongoing need for flame retardant, also referred to as fire resistant, fabrics that can be used to make clothing suitable for people who work near flames, high temperatures, or electric arc flashes. In addition to showing excellent thermal performance, an effective flame retardant fabric should be durable, comfortable, and produced at low cost.
- 10 Although fabrics made of inherently flame retardant fibers have been very useful in protective garments, certain characteristics of these fibers present problems. For instance, these fibers can be difficult to dye, provide uncomfortable fabric textures, and are expensive. To address these problems, inherently flame retardant fibers have been blended with
- 15 fibers made of other materials. Fiber blending can be used to obtain an end fabric that combines the beneficial characteristics of each of the constituent fibers. However, such blending often comes at the expense of durability and thermal performance.

 Certain fiber blends and fabrics made from those blends are known in the art. For instance, U.S. Patent No. 4,920,000 (Green) issued on April 24, 1990 discloses a durable heat resistant fabric comprising certain blends of cotton, nylon, and heat resistant fibers. U.S. Patent No. 6,132,476 (Lunsford et al.) issued October 17, 2000 discloses dyed fabric blends containing inherently flame retardant fibers and flame retardant cellulose fibers containing a flame retardant compound. U.S. Patent No. 6,254,988 B1 (Zhu et al.) issued on July 3, 2001 discloses a fabric composed of particular blends of cotton, nylon, and para-aramid fibers that is comfortable, cut resistant, and abrasion resistant. U.S. Patent Application Publication No. 2001/0009832 A1 (Shaffer et al.) published on July 26, 2001 discloses a flame retardant fabric comprising dissimilar warp and fill yarns wherein the warp yarns comprise staple or filament fibers and have a Limiting Oxygen Index of at least 27, the fill yarns comprise natural fibers, and the ratio of warp to fill yarn ends in the fabric is at least

1.0. U.S. Patent No. 6,547,835 B1 (Lunsford et al.) issued on April 15, 2003 discloses a method for dyeing flame retardant fabrics.

Fabrics made from the fiber blends and yarns discussed above either naturally suffer from poor resistance to abrasion or, as disclosed in

- 5 U.S. Patent No. 4,920,000 (Green) issued on April 24, 1990, utilize a large percentage of cotton fiber, which has very low abrasion resistance. Fire protective clothing and garments are normally used in harsh environments so any improvement in abrasion resistance of the fabrics used in those garments is important and desired. There is therefore, a need for flame
10 retardant fiber blends, yarns, and fabrics that have improved abrasion resistance.

SUMMARY OF THE INVENTION

In accordance with the purpose of the invention, as embodied and broadly described herein, the invention is an intimate blend of staple fibers comprising 10 to 75 parts by weight of at least one aramid staple fiber, 15 to 80 parts by weight of at least one flame retardant cellulosic staple fiber, and 5 to 30 parts by weight of at least one polyamide staple fiber.

- 15 In another embodiment, the invention is an intimate blend of staple fibers comprising 20 to 40 parts by weight of at least one aramid staple
20 fiber, 50 to 80 parts by weight of at least one flame retardant cellulosic staple fiber, and 15 to 20 parts by weight of at least one polyamide staple fiber.

- 25 In another embodiment, the invention is one of the intimate blends described above, wherein the at least one aramid staple fiber is poly(metaphenylene isophthalamide) and the at least one flame retardant cellulosic staple fiber is flame retardant rayon.

- 30 In another embodiment, the invention is one of the intimate blends described above, wherein the at least one aramid staple fiber is poly(metaphenylene isophthalamide) and the at least one flame retardant cellulosic staple fiber comprises silicon dioxide in the form of polysilicic acid in a cellulose supporting structure and the silicon dioxide in the form of polysilicic acid in a cellulose supporting structure is present in an amount of no more than 40 percent by weight of the intimate blend.

The intimate blends of this invention may be used to make a yarn, which in turn may be used to make a flame retardant fabric for use in flame retardant articles such as clothing.

Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating embodiments of the invention, are given by way of illustration only, because various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DETAILED DESCRIPTION

There is an ongoing need for fiber blends from which flame retardant, also referred to as fire resistant, fabrics can be made that can be used to make clothing and other articles suitable for people who work near flames, high temperatures, or electric arc flashes and the like. Considerable effort has been made to increase the effectiveness of such fiber blends and the resulting fabrics, while maintaining or improving their comfort and durability and reducing their overall cost. The present invention represents just such an advance in the field of flame retardant garments.

An intimate blend of staple fibers of this invention comprises aramid fibers, flame retardant cellulosic fibers, and polyamide fibers. The proportions of each component are important to achieve the necessary combination of physical qualities. By "intimate blend" is meant that two or more fiber classes are blended prior to spinning a yarn. In the present invention, the intimate blend is formed by combining aramid fibers, flame retardant cellulosic fibers, and polyamide fibers in the fiber form, and then spinning into a single strand of yarn. By "yarn" is meant an assemblage of fibers spun or twisted together to form a continuous strand, which can be used in weaving, knitting, braiding, or plaiting, or otherwise made into a

textile material or fabric. Such yarns can be made by conventional methods for spinning staple fibers into yarns, such as, for example, ring-spinning, or higher speed air spinning techniques such as Murata air-jet spinning where air is used to twist the staple into a yarn.

- 5 The intimate blend of staple fibers of this invention includes aramid fibers, which are inherently flame retardant. By "aramid fiber" is meant one or more fibers made from one or more aromatic polyamides, wherein at least 85% of the amide (-CONH-) linkages are attached directly to two aromatic rings. Aromatic polyamides are formed by reactions of aromatic
10 diacid chlorides with aromatic diamines to produce amide linkages in an amide solvent. Aramid fibers may be spun by dry or wet spinning using any number of processes, however, U.S. Patent Nos. 3,063,966; 3,227,793; 3,287,324; 3,414,645; 3,869,430; 3,869,429; 3,767,756; and 5,667,743 are illustrative of useful spinning processes for making fibers
15 that could be used in this invention.

Aramid fibers are typically available in two distinct classes, namely meta-aramid fibers, or m-aramid fibers, one of which is composed of poly(metaphenylene isophthalamide), which is also referred to as MPD-I, and para-aramid fibers, or p-aramid fibers, one of which is composed of poly(paraphenylene terephthalamide), also referred to as PPD-T. Meta-aramid fibers are currently available from E.I. DuPont de Nemours of Wilmington, Delaware in several forms under the trademark NOMEX®: NOMEX T-450® is 100% meta-aramid; NOMEX T-455® is a blend of 95% NOMEX® and 5% KEVLAR® (para-aramid); and NOMEX IIIA® (also known as NOMEX T-462®) is 93% NOMEX®, 5% KEVLAR®, and 2% carbon core nylon. In addition, meta-aramid fibers are available under the trademarks CONEX® and APYEIL® which are produced by Teijin, Ltd. of Tokyo, Japan and Unitika, Ltd. of Osaka, Japan, respectively. Para-aramid fibers are currently available under the trademarks KEVLAR® from
20 E.I. DuPont de Nemours of Wilmington, Delaware and TWARON® from Teijin Ltd. of Tokyo, Japan. For the purposes herein, TECHNORA® fiber, which is available from Teijin Ltd. of Tokyo, Japan, and is made from
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copoly(p-phenylene/3,4'diphenyl ester terephthalamide), is considered a para-aramid fiber.

In one embodiment of this invention, the at least one aramid staple fiber is poly(metaphenylene isophthalamide).

5 The intimate blend of staple fibers of this invention also includes flame retardant cellulosic fibers. Flame retardant cellulosic staple fibers are comprised of one or more cellulosic fibers and one or more flame retardant compounds. Cellulosic fibers, such as rayon, acetate, triacetate, and lyocell, which are generic terms for fibers derived from cellulose, are
10 well-known in the art.

Cellulosic fibers, although softer and less expensive than inherently flame retardant fibers, are not naturally resistant to flames. To increase the flame retarding capability of these fibers, one or more flame retardants are incorporated into or with the cellulosic fibers. Such flame retardants
15 can be incorporated by spinning the flame retardant into the cellulosic fiber, coating the cellulosic fiber with the flame retardant, contacting the cellulosic fiber with the flame retardant and allowing the cellulosic fiber to absorb the flame retardant, or any other process that incorporates a flame retardant into or with a cellulosic fiber. There are a variety of such flame
20 retardants, including, for example, certain phosphorus compounds, like SANDOLAST 9000®, currently available from Sandoz, certain antimony compounds, and the like. Generally speaking, cellulosic fibers which contain one or more flame retardants are given the designation "FR," for flame retardant. Accordingly, flame retardant cellulosic fibers such as FR
25 rayon, FR acetate, FR triacetate, and FR lyocell may be used in the present invention. Flame retardant cellulosic fibers are also available under various trademarks, such as VISIL®, which is available from Sateri Oy of Finland. VISIL® fiber contains silicon dioxide in the form of polysilicic acid in a cellulose supporting structure wherein the polysilicic
30 acid contains aluminum silicate sites. When the intimate blends of this invention comprise VISIL® fibers, the VISIL® fibers should be present in an amount of no more than 40 percent by weight of the intimate blend.

Methods for making flame retardant cellulosic fibers are generally disclosed in, for example, U.S. Patent No. 5,417,752.

In one embodiment of this invention, the at least one flame retardant cellulosic fiber is flame retardant rayon. Rayon is well-known in
5 the art, and is a generic term for filaments made from various solutions of modified cellulose by pressing or drawing the cellulose solution. The cellulose base for the manufacture of rayon is obtained from wood pulp.

In another embodiment of this invention the at least one flame retardant cellulosic staple fiber comprises silicon dioxide in the form of
10 polysilicic acid in a cellulose supporting structure and the silicon dioxide in the form of polysilicic acid in a cellulose supporting structure is present in an amount of no more than 40 percent by weight of the intimate blend.

The intimate blend of staple fibers of this invention also includes polyamide fibers. By "polyamide fibers" is meant one or more fibers made
15 from one or more aliphatic polyamide polymers, generically referred to as nylon. Examples include polyhexamethylene adipamide (nylon 66), polycaprolactam (nylon 6), polybutyrolactam (nylon 4), poly(9-aminononanoic acid) (nylon 9), polyenantholactam (nylon 7), polycapryllactam (nylon 8), and polyhexamethylene sebacamide (nylon 6,
20 10). Nylon fibers are generally spun by extrusion of a melt of the polymer through a capillary into a gaseous congealing medium. When nylon is the polyamide fiber in the intimate blend of staple fibers forming a yarn, such yarn preferably is used as the warp yarn when forming a fabric to enhance protection against soft surface abrasion in the finished fabric or garment
25 made from such fabric. In one embodiment of this invention, when nylon is used in this manner to make the fabrics or garments of this invention, the fabrics or garments of this invention are expected to have more than ten percent higher resistance to abrasion compared to similar fabrics without nylon, as measured in cycles to failure according to the Abrasion
30 Resistance Test described below. However, too much nylon in a fabric will cause the fabric to become stiff and lose drape when the fabric is exposed briefly to high temperatures.

In one embodiment of this invention, nylon fiber has a linear density from 1 to 3 dtex. In another embodiment the nylon fiber has a linear density from 1 to 1.5 dtex. In yet another embodiment the nylon fiber has a linear density of about 1.1 dtex.

- 5 The intimate blend of staple fibers of this invention can be used to make yarns and fabrics that are flame retardant. These yarns and fabrics can be used to make flame retardant articles, such as flame retardant garments and clothing, which are particularly useful for firefighters and other workers who are put in close proximity to flames, high temperatures,
- 10 or electric arc flashes. Generally, by "flame retardant" is meant that the fabric does not support flame in air after coming in contact with a flame for a short period of time. More precisely, "flame retardant" can be defined in terms of the Vertical Flame Test, described below. Flame retardant fabrics preferably have a char length of less than six inches after a twelve
- 15 second exposure to a flame. The terms "flame retardant," "flame resistant," "fire retardant," and "fire resistant" are used interchangeably in the industry, and references to "flame retardant" compounds, fibers, yarns, fabric, and garments in the present invention could be described identically as "flame resistant," "fire retardant," or "fire resistant."
- 20 Staple fibers for use in spinning yarns are generally of a particular length and of a particular linear density. For use in this invention, synthetic fiber staple lengths of 2.5 to 15 centimeters (1 to 6 inches) and as long as 25 centimeters (10 inches) can be used, and lengths of 3.8 to 11.4 centimeters (1.5 to 4.5 inches) are preferred. Yarns made from such
- 25 fibers having staple lengths of less than 2.5 centimeters have been found to require excessively high levels of twist to maintain strength for processing. Yarns made from such fibers having staple lengths of more than 15 centimeters are more difficult to make due to the tendency for long staple fibers to become entangled and broken, resulting in short fibers.
- 30 The synthetic staple fibers can be crimped or not, as desired for any particular purpose. The staple fibers of this invention are generally made by cutting continuous filaments to certain predetermined lengths. However, staple fibers can be made by other means, such as by stretch-

breaking, and yarns can be made from such fibers as well as from a variety or distribution of different staple fiber lengths.

In one embodiment of this invention, the yarn of this invention can be used to make a flame retardant fabric, which is a cloth produced by weaving, knitting, or otherwise combining the yarn of this invention. Flame retardant fabrics can be constructed having warp yarn comprising the yarns of this invention, fill yarn comprising the yarns of this invention, or both warp and fill yarns comprising the yarns of this invention. When fabrics use the yarn of this invention in only one direction (i.e., as only fill or only warp), other suitable yarns may be used in the other direction according to the desired fabric characteristics. For best abrasion resistance, the yarn of this invention is used in the warp direction since warp yarn typically forms most of the direct contact surface of a fabric. This translates into better abrasion performance of the outer surface of the fabric in garment form.

In one embodiment of this invention, the flame retardant fabric has a basis weight of from 4 and 15 ounces per square yard. In another embodiment of this invention the flame retardant fabric has a basis weight of from 5.5 to 11 ounces per square yard. Such fabrics can be made into articles of clothing, such as shirts, pants, coveralls, aprons, jacket, or any other single or multi-layer form for flash fire or electric arc protection.

The articles of the invention will be further described below with reference to the working examples. It should be noted however that the concept of the invention will not be limited at all by these examples.

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TEST METHODS

The following test methods were used in the following Examples.

Thermal Protective Performance Test (TPP)

30 The predicted protective performance of a fabric in heat and flame was measured using the "Thermal Protective Performance Test" (NFPA 2112). A flame was directed at a section of fabric mounted in a horizontal position at a specified heat flux (typically 84 kW/m²). The test measures the transmitted heat energy from the source through the specimen using a

copper slug calorimeter with no space between the fabric and heat source. The test endpoint was characterized by the time required to attain a predicted second-degree skin burn injury using a simplified model developed by Stoll & Chianta, "Transactions New York Academy Science", 5 1971, 33 p 649. The value assigned to a specimen in this test, denoted as the "TPP value," is the total heat energy required to attain the endpoint, or the direct heat source exposure time to the predicted burn injury multiplied by the incident heat flux. Higher TPP values denote better insulation performance.

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Vertical Flame Test

The "Vertical Flame Test" (ASTM D6413) is generally used as a screening test to determine whether a fabric burns, as a predictor for whether an article of clothing has any flame retarding properties. 15 According to the test, a 3 x 12 inch section of fabric was mounted vertically and a specified flame was applied to its lower edge for twelve seconds. The response of the fabric to the flame exposure was recorded. The length of the fabric that was burned or charred was measured. Times for afterflame (i.e., the continued burning of the fabric section after removing 20 the test flame) and afterglow (characterized by smoldering of the fabric section after removing the test flame) were also measured. Additionally, observations regarding melting and dripping from the fabric section were recorded. Pass/fail specifications based on this method are known for industrial worker clothing, firefighter turnout gear and flame retardant 25 station wear, and military clothing. According to industry standards, a fabric can be considered flame retardant, or fire resistant, if it has a char length of less than six inches after a twelve second exposure to a flame.

Abrasion Resistance Test

30 Abrasion resistance was determined using ASTM method D3884, with a H-18 wheel, 500 gms load on a Taber abrasion resistance meter available from Teledyne Taber, 455 Bryant St., North Tonawanda, N.Y. 14120. Taber abrasion resistance was reported as cycles to failure.

Tear Strength Test

The tear strength measurement is based on ASTM D 5587. The tear strength of textile fabrics was measured by the trapezoid procedure using a recording constant-rate-of-extension-type (CRE) tensile testing machine. Tear strength, as measured in this test method, requires that the tear be initiated before testing. The specimen was slit at the center of the smallest base of the trapezoid to start the tear. The nonparallel sides of the marked trapezoid were clamped in parallel jaws of a tensile testing machine. The separation of the jaws was increased continuously to apply a force to propagate the tear across the specimen. At the same time, the force developed was recorded. The force to continue the tear was calculated from autographic chart recorders or microprocessor data collection systems. Two calculations for trapezoid tearing strength were provided: the single-peak force and the average of five highest peak forces. For the examples here, the single-peak force was used.

Grab Strength Test

The grab strength measurement, which is a determination of breaking strength and elongation of fabric or other sheet materials, is based on ASTM D5034. A 100 mm (4.0 in.) wide specimen was mounted centrally in clamps of a tensile testing machine and a force applied until the specimen broke. Values for the breaking force and the elongation of the test specimen were obtained from machine scales or a computer interfaced with testing machine.

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EXAMPLES

Example 1

A comfortable and durable fabric was prepared from warp yarns comprising an intimate blend of NOMEX® type 462 staple fiber, flame retardant (FR) rayon staple fiber, and nylon staple fiber, and fill yarns comprising an intimate blend of FR rayon staple fiber and nylon staple fiber. NOMEX® type 462 is 93% by weight of poly(m-phenylene isophthalamide)(MPD-I) staple fiber, 5% by weight poly(p-phenylene terephthalamide)(PPD-T) staple fiber, and 2% by weight carbon-core

nylon-sheath static dissipative staple fibers (Type P-140 available from E.I. DuPont de Nemours of Wilmington, Delaware). FR rayon is a cellulosic fiber containing a flame retardant compound, and the nylon was polyhexamethylene adipamide. A picker blend sliver of 40 weight percent 5 of NOMEX® type 462 staple fiber, 45 weight percent of FR rayon staple fiber and 15 weight percent of nylon staple fiber was prepared and processed by the conventional cotton system into a spun yarn having twist multiplier of 3.5 using a ring spinning frame. The yarn so made was a 10 19.7 tex (30 cotton count) single yarn. Two single yarns were then plied 15 on a plying machine to make a two-ply yarn. Using a similar process and the same twist and yarn density, a blend of 75 weight percent of FR rayon staple fiber and 25 weight percent nylon fiber was used to make a two-ply 20 yarn.

The NOMEX®/FR rayon/nylon yarn was used as the warp yarn and 15 FR rayon/nylon yarn was used as the fill yarn in a shuttle loom in a 3x1 twill construction. The greige twill fabric had a construction of 36 ends x 22 picks per cm (92 ends x 57 picks per inch), and basis weight of 323 g/m² (9.7 oz/yd²). The greige twill fabric prepared as described above was scoured in hot water and dried under low tension. The scoured fabric was 20 then dyed using acid dye. The finished fabric was then tested for its thermal and mechanical properties. The results of these tests are shown in Table 1.

Table 1. Example 1 Test Results

Fabric Design	Warp Yarn	NOMEX®/FR Rayon/Nylon 40/45/15 % by Weight
	Fill Yarn	FR Rayon/Nylon 75/25 % by Weight
Test Description	Units	Value
Basis Weight	oz/y ²	9.7
Yarn Size	count (warp×fill)	30/2x30/2
TPP	cal/cm ²	17.2
Vertical Flame Char	inch (warp×fill)	4.7x2.4
Abrasion	Cycle	1578
Tear Resistance	lbf (warp×fill)	26.6x11.0
Grab Strength	lbf (warp×fill)	191.0x97.8

Example 2

A comfortable and durable fabric was prepared as in Example 1, however, the warp yarns were made from 20 weight percent of NOMEX® type 462 staple fiber, 55 weight percent of FR rayon staple fiber, and 25 5 weight percent of nylon staple fiber, the spun yarns having a twist multiplier of 3.7. The yarn so made was a 24.6 tex (24 cotton count) single yarn. Two single yarns were then plied on the plying machine to make a two-ply yarn. Using a similar process and the same twist as in Example 1, a single yarn was made comprising a blend of 20 weight 10 percent NOMEX® type 462 staple fiber and 80 weight percent FR rayon staple fiber, having a linear density of 32.8 tex (18 cotton count). Two of these yarns were then plied to form a ply yarn.

The NOMEX®/FR rayon/Nylon yarn and NOMEX®/FR rayon yarn were used as the warp and fill, respectively, in a shuttle loom in a 3x1 twill 15 construction. The greige twill fabric had a construction of 26 ends x 17 picks per cm (66 ends x 44 picks per inch), and basis weight of 323 g/m² (9.7 oz/yd²). The greige twill fabric prepared as described above was scoured in hot water and dried under low tension. The scoured fabric was then dyed using acid dye. The finished fabric was tested for its thermal 20 and mechanical properties. The results of these tests are shown in Table 2.

Table 2. Example 2 Test Results

Fabric Design	Warp Yarn	NOMEX®/FR Rayon/Nylon 20/55/25 % by Weight
	Fill Yarn	NOMEX®/FR Rayon 20/80 % by Weight
Test Description	Units	Value
Basis Weight	oz/y ²	9.7
Yarn Size	count (warp×fill)	24/2x18/2
TPP	cal/cm ²	16.9
Vertical Flame Char	inch (warp×fill)	1.0x1.3
Abrasion	Cycle	784
Tear Resistance	lbf (warp×fill)	18.3x14.8
Grab Strength	lbf (warp×fill)	121.1x124.9

Example 3

A fabric was prepared as in Example 1, however, both the warp and fill yarns were made from 50 weight percent of NOMEX® type 462 staple fiber, 35 weight percent of VISIL® staple fiber, and 15 weight percent of 5 nylon staple fiber, the spun yarns having a twist multiplier of 3.7. The yarn so made was a 24.6 tex (24 cotton count) single yarn. Two of these yarns were then plied on the plying machine to make a two-ply yarn. Using the same fiber composition, process, and twist multiplier, a single yarn of 32.8 tex (18 cotton count) was made. Two of these were then plied to form a 10 ply yarn.

The NOMEX®/VISIL®/nylon yarns were used as the warp and fill in a shuttle loom in a 3x1 twill construction. The greige twill fabric had a construction of 23 ends x 16 picks per cm (58 ends x 40 picks per inch), and basis weight of 247.5 g/m² (7.3 oz/yd²). The greige twill fabric 15 prepared as described above was scoured in hot water and dried under low tension. The scoured fabric was then dyed using acid dye. The finished fabric was tested for its thermal and mechanical properties. The results of these tests are shown in Table 3.

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Table 3. Example 3 Test Results

Fabric Design	Warp Yarn	NOMEX®/VISIL®/Nylon 50/35/15 % by Weight
	Fill Yarn	NOMEX®/VISIL®/Nylon 50/35/15 % by Weight
Test Description	Units	Value
Basis Weight	oz/y ²	7.3
Yarn Size	count (warp×fill)	24/2×18/2
TPP	cal/cm ²	14.4
Vertical Flame Char	inch (warp×fill)	3.7×3.2
Abrasion	Cycle	558
Tear Resistance	lbf (warp×fill)	30.1×34.2
Grab Strength	lbf (warp×fill)	157.1×168.7